

PTO 08-6602

JP
20000215
Kokai
12042755

HEAT-RESISTANT NI-BASED ALLOY BONDING METHOD
[Tainetsu Ni ki no gokin no setsuko hoho]

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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. JULY 2008
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	12042755
DOCUMENT KIND	(12):	Kokai
PUBLICATION DATE	(43):	20000215
APPLICATION NUMBER	(21):	10215739
APPLICATION DATE	(22):	19980730
INTERNATIONAL CLASSIFICATION ⁷	(51):	B 23 K 20/00 20/14 31/00
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TITLE	(54):	HEAT-RESISTANT NI-BASED ALLOY BONDING METHOD
FOREIGN TITLE	[54A]:	Tainetsu Ni ki no gokin no setsuko hoho

1. A heat-resistant Ni-based alloy bonding method that uses an Ni-based alloy containing Al: 1.5-15 wt% and having excellent high-temperature strength and corrosion resistance as the material to bond, characterized by the following facts: the bonding surfaces of the materials to bond are abutted against each other via an insertion material made of an Ni-based alloy containing Cr: 1-18%, B: 1-5%, Ce: 0.01-5%, and Zr: 0-11%, Hf: 0-22%, Nb: 0-11%, Ta: 0-22% in wt%; in a vacuum atmosphere of 8×10^{-1} torr or lower or a shield atmosphere formed by an inactive gas containing 0-5 vol% of hydrogen, in the state when a pressure of 0.1-2.0 kgf/mm² is applied in the abutting direction, the abutted parts are kept at a temperature higher than the melting point of the insertion material but lower than the melting point of the material to bond for at least 120 sec to perform diffusion bonding.

2. The heat-resistant Ni-based alloy bonding method described in Claim 1 characterized by the fact that a post heat treatment is performed at a specific temperature T (°C) in the range of 1100-1350°C for a period of time t (s) that satisfies $(T+273) \times (\log(t/3600) + 20) \times 10^{-3} \leq 33$ in the joint part after the diffusion bonding.

3. The heat-resistant Ni-based alloy bonding method described in Claim 1 or 2 characterized by the fact that the material to bond is a Ni-based alloy containing C: 0.1% or less, Si: 5% or less, Mn: 0.2% or less, Cr: 1-18%, Al: 1.5-15%, Fe: 0-5%, B: 0-0.05%, Zr: 0-0.5%, Hf: 0-1%, Ti: 0-1%, Mg: 0-0.05%, Mo: 0-6%, W: 0-12%, V: 0-3.5%, Nb: 0-5.5%, Ta: 0-11%, Y: 0-0.25%, La: 0-0.25%, and Ce: 0-0.25% in wt%.

* [Numbers in right margin indicate pagination of the original text.]

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention pertains to method for bonding heat-resistant Ni-based alloy with excellent strength and corrosion resistance at a high temperature around 1000°C. In particular, the present invention pertains to a bonding method for heat-resistant pressure-proof pipelines in petrochemical plants.

[0002]

Prior art

Austenite type stainless steel having high Cr content and/or high Ni content has been used for heat-resistant pressure-proof pipelines in petrochemical plants. Recently, [the use of] Ni-based alloy with increased Al content to improve high-temperature strength and corrosion resistance to withstand severe use conditions has been proposed (for example, Japanese Kokai Patent Application No. Hei 4[1992]-358037, Hei 5[1993]-33090, Hei 5[1993]-33091, and Hei 5[1993]-33092).

[0003]

When said alloy containing large amount of Al is assembled as structural parts, if gas tungsten arc welding method (GTAW method: so-called TIG welding method) is used, cracks will occur at high temperature, or thermal cracks will occur again during the heat treatment performed after welding. If the wax attaching method is used, due to formation of Al_2O_3 film, good wettability cannot be realized on the bonding surface. As a result, bonding defects will occur. Therefore, even if the pipes are bonded, since a

fragile intermetallic compound phase is formed as an abnormal phase in the bonded layer, it is not possible to obtain good high-temperature strength.

[0004]

If the solid-phase diffusion bonding method is used, good contact between bonding surfaces cannot be realized due to the Al_2O_3 film formed on the bonding surfaces. As a result, bonding defects tend to occur. Therefore, good high-temperature strength cannot be obtained, and it is difficult to use such an alloy in structural parts. On the other hand, liquid phase diffusion bonding method is known as a method for preventing generation of fragile intermetallic compound phase in the bonded part (for example, Japanese Kokoku Patent No. Hei 3[1991]-71950). For high Al alloy, however, similar to the case of wax attachment, since Al_2O_3 film is formed, the insertion material in liquid phase cannot be spread uniformly on the bonding surface. As a result, a high-quality bonded part cannot be obtained.

[0005]

Problems to be solve by the invention

The objective of the present invention is to provide a heat-resistant Ni-based alloy bonding method realized by diffusion bonding, which can guarantee obtaining a creep strength comparable to that of the mother material at a high temperature around 1000°C in the bonded part using a Ni-based alloy having a high Al content as the material to bond.

[0006]

Means to solve the problem

The present inventors have conducted research to establish a liquid phase diffusion bonding technology for Ni-based heat-resistant alloy having a high Al content and have confirmed the following items.

[0007]

(a) Chemical composition of insertion material

The insertion material should be the following Ni-based alloy in order to guarantee strength and corrosion resistance at high temperature.

[0008]

B is an essential element with significant effect on lowering the melting point of the insertion material.

[0009]

Cr is needed to guarantee strength and corrosion resistance at high temperature. Cr has little effect on the melting point of the insertion material and the bonding defect percentage.

[0010]

Ce is an essential element used for improving the wettability between the bonding surface and the melted insertion material to lower the bonding defect percentage.

[0011]

Zr, Hf, Ta, Nb can be added as needed since they can improve the wettability between the bonding surface and the melted insertion material to lower the bonding defect percentage although addition of these elements will increase the melting point of the insertion material.

[0012]

In consideration of the aforementioned facts, an Ni-based alloy containing Cr: 1-18%, B: 1-5%, Ce: 0.01-5%, and Zr: 0-11%, Hf: 0-22%, Nb: 0-11%, Ta: 0-22% is used as the insertion material.

[0013]

(b) Bonding conditions

The result of studying (1) atmosphere during bonding, (2) bonding time, and (3) bonding pressure shows that it is necessary to adopt the following bonding conditions in order to obtain bonded part with good properties and free of bonding defect. /3

[0014]

(c) Conditions of the post heat treatment

When a post heat treatment is performed on the bonded part (referred to as joint or joint part hereinafter obtained under conditions that satisfy said (a), (b), the creep strength at high temperature can be further improved.

[0015]

The present invention was completed through trial production of plural joints on site based on the aforementioned facts. The result is the heat-resistant Ni-based alloy bonding method of (1) and (2) below.

[0016]

(1) A heat-resistant Ni-based alloy bonding method that uses an Ni-based alloy containing Al: 1.5-15 wt% and having excellent high-temperature strength and corrosion resistance as the material to bond, characterized by the following facts: the bonding surfaces of the materials to bond are abutted against each other via an insertion material made of an Ni-based alloy containing Cr: 1-18%, B: 1-5%, Ce: 0.01-5%, and Zr: 0-11%, Hf: 0-22%, Nb: 0-11%, Ta: 0-22% in wt%; in a vacuum atmosphere of 8×10^{-1} torr or lower or a shield atmosphere formed by an inactive gas containing 0-5 vol% of hydrogen, in the state when a pressure of 0.1-2.0 kgf/mm² is applied in the abutting direction, the abutted parts are kept at a temperature higher than the melting point of the insertion material but lower than the melting point of the material to bond for at least 120 sec to perform diffusion bonding.

[0017]

(2) The heat-resistant Ni-based alloy bonding method described in said (1) characterized by the fact that a post heat treatment is performed at a specific temperature T (°C) in the range of 1100-1350°C for a period of time t (s) that satisfies $(T+273) \times (\log(t/3600) + 20) \times 10^{-3} \leq 33$ in the joint part after the diffusion bonding.

[0018]

In the present invention of said (1) and (2), the material to bond can be an Ni-based alloy containing 1.5-15 wt% of Al. However, the material to bond is preferred to be a Ni-based alloy containing C: 0.1% or less, Si: 5% or less, Mn: 0.2% or less, Cr: 1-18%, Al: 1.5-15%, Fe: 0-5%, B: 0-0.05%, Zr: 0-0.5%, Hf: 0-1%, Ti: 0-1%, Mg: 0-0.05%, Mo: 0-6%, W: 0-12%, V: 0-3.5%, Nb: 0-5.5%, Ta: 0-11%, Y: 0-0.25%, La: 0-0.25%, and Ce: 0-0.25% in wt%.

[0019]

The Ni-based alloy as the material to bond can have a form of pipe, thick plate, sheet, or forged product. The insertion material can be a thin band with a thickness of 5-500 μm . In the case of bonding pipelines, the area around the bonded part on the cross section where the pipelines will be bonded is covered. Said coverage can be formed in a concentric ring shape to reduce unnecessary coverage. The inactive gas refers to Ar, N₂, or other gas that is difficult to oxidize.

[0020]

Embodiment of the invention

In the following, the reasons for restricting the bonding method of the present invention as described above will be explained. IN the following explanation, "%" means "wt%" for metal elements.

[0021]

Insertion material

The insertion material can use a commercially available product (name "Glassmet"). It can be manufactured by dripping melted alloy (Ni-based alloy) with adjusted composition on a rotary roll surface using double roll method or single roll method. The chemical composition is as follows.

[0022]

Cr: 1-18%

Cr can effectively improve the strength and corrosion resistance at high temperature. Its content must be 1% or more. However, if the content is more than 18%, the structure stability and the high-temperature creep strength will deteriorate. Therefore, the content of Cr should be in the range of 1-18%, preferably, in the range of 2-16% so that better corrosion resistance and strength can be guaranteed.

[0023]

B: 1-5%

B is effective on lowering the melting point of the insertion material. Its content must be 1% or more. However, if the content is more than 5%, generation of boride in the bonding layer will be assisted to lower the ductility of the bonded part. Therefore, the content of B should be in the range of 1-5%, preferably, in the range of 1.5-4.5%.

[0024]

Ce: 0.01-5%

Ce has strong affinity to oxygen (O) and can break Al_2O_3 film. Therefore, it is an element effective on improving the wettability to lower the bonding defect percentage. In order to obtain said effect, its content must be 0.01% or more. However, if its content is more than 5%, it will react with mother material Al to generate Al-Ce intermetallic compound. As a result, the ductility, strength of the bonded part will degrade, and the insertion material itself will be difficult to manufacture. Therefore, the content of Ce should be in the range of 0.01-5%, preferably, in the range of 0.1-4%.

[0025]

Zr: 0-11%

The material may not contain Zr. If it is added, Zr will reinforce the affinity with oxygen (O) to brake Al_2O_3 film to improve the wettability so that the bonding defect percentage can be lowered. In order to obtain said effect, its content must be 0.01% or more. However, if its content is more than 11%, it will react with mother material Al to generate Al-Zr intermetallic compound. As a result, the ductility, strength of the bonded part will degrade, and the insertion material itself will be difficult to manufacture. Therefore, the content of Zr should be in the range of 0.01-11%.

[0026]

Hf: 0-22%

The material may not contain Hf. If it is added, Hf will reinforce the affinity with oxygen (O) to brake Al_2O_3 film to improve the wettability so that the bonding defect percentage can be lowered. In order to obtain said effect, its content must be 0.01% or more. However, if its content is more than 22%,

it will react with mother material Al to generate Al-Hf intermetallic compound. As a result, the ductility, strength of the bonded part will degrade, and the insertion material itself will be difficult to manufacture.

Therefore, the content of Hf should be in the range of 0.01-22%.

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[0027]

Nb: 0-11%

The material may not contain Nb. If it is added, Nb will reinforce the affinity with oxygen (O) to brake Al_2O_3 film to improve the wettability so that the bonding defect percentage can be lowered. In order to obtain said effect, its content must be 0.01% or more. However, if its content is more than 11%, it will react with mother material Al to generate an Al-Nb intermetallic compound. As a result, the ductility, strength of the bonded part will degrade, and the insertion material itself will be difficult to manufacture. Therefore, the content of Nb should be in the range of 0.01-11%.

[0028]

Ta: 0-22%

The material may not contain Ta. If it is added, Ta will reinforce the affinity with oxygen (O) to brake Al_2O_3 film to improve the wettability so that the bonding defect percentage can be lowered. In order to obtain said effect, its content must be 0.01% or more. However, if its content is more than 22%, it will react with mother material Al to generate Al-Ta intermetallic compound. As a result, the ductility, and strength of the bonded part will degrade, and the insertion material itself will be difficult to manufacture. Therefore, the content of Ta should be in the range of 0.01-22%.

[0029]

Other Ni-based alloys containing normally used alloy elements that will not adversely affect the strength or corrosion resistance at high temperature are also included in the scope of the present invention. It is acceptable that inevitable [minor] impurities are contained in the normal ranges.

[0030]

Chemical composition of the material to bond

In invention 1, an Ni-based alloy with excellent high-temperature strength and corrosion resistance is used as the material to bond since it is used in chemical plants exposed to high-temperature environment. The Ni-based alloy is an alloy having a high content of Ni since it has excellent high-temperature strength and high-temperature corrosion resistance.

[0031]

Al: 1.5-15%

Al is needed to improve the anti-carburization property and the anti-coking property at high temperatures. Therefore, the Ni-based alloy as the object of the present invention must contain 1.5% or more of Al. However, if the content is more than 15%, the ductility and tenacity at normal temperature and high temperature will deteriorate. Therefore, the Al content should be in the range of 1.5-15%, preferably, in the range of 4-13%.

[0032]

Other alloy elements are preferred to have the following contents.

[0033]

C: 0.1% or less

If added in a minute amount, C is an element effective on guaranteeing the strength at normal temperature and high temperature. However, if the content is more than 0.1%, the ductility and tenacity will degraded. Therefore, the upper limit of the content is 0.1%. In order to guarantee the strength, the content is preferred to be 0.003% or more. Usually, the C content will not be less than 0.003%.

[0034]

Si: 5% or less

As a deoxidation element, Si can also improve the anti-oxidation property or the anti-carburization property in some cases. However, if the content is more than 5%, the ductility and the tenacity will degrade significantly. Therefore, the upper limit of its content is 5%. In order to realize the deoxidation effect, the lower limit of the Si content is around 0.05%.

[0035]

Mn: 0.2% or less

Although Mn has deoxidation effect, it will accelerate formation of spinel type oxide film that will degrade the anti-coking property. Therefore, the upper limit of its content should be 0.2%, preferably, 0.1%.

[0036]

Cr: 1-18%

In order to guarantee the anti-oxidation property and the anti-coking property, 1% or more of Cr is needed. However, there is no need for the Ni-based alloy with high Al content used as the material to bond to contain this element at high concentration. If its content is more than 18%, the stability of the texture at high temperature will degrade, and carbide will be deposited unevenly to degrade the tenacity. Therefore, the content of Cr should be in the range of 1-18%, preferably, in the range of 3-15%.

[0037]

Fe: 0-5%

The alloy usually contains no Fe. If it is added, Fe will substitute a part of expensive Ni. Although iron cannot replace Ni to improve the properties, it will not cause deterioration, either. However, if the content is more than 5%, the heat resistance will deteriorate. Therefore, the upper limit of the Fe content if it is added is 5%.

[0038]

B: 0-0.05%

The alloy usually contains no B. B can reinforce the boundaries between crystalline particles to improve the creep strength. This effect becomes significant when its content becomes 0.001% or more. However, if its content is more than 0.05%, the creep strength will drop. Therefore, if it is added, the content of B is preferred to be in the range of 0.001-0.05%.

[0039]

Zr: 0-0.5%

The alloy usually contains no Zr. Zr can reinforce the boundaries between crystalline particles to improve the creep strength. This effect becomes significant when its content becomes 0.001% or more. However, if its content is more than 0.5%, coarse carbide will be generated, and the creep strength will drop. Therefore, if it is added, the content of Zr is preferred to be in the range of 0.01-0.05%.

[0040]

Hf: 0-1%

The alloy usually contains no Hf. Hf can reinforce the boundaries between crystalline particles to improve the creep strength. This effect becomes significant when the content is 0.05% or more. However, if the content is more than 1%, coarse carbide will be generated, and the creep strength will drop. Therefore, if it is added, the content of Hf is preferred to be in the range of 0.05-1%.

[0041]

Mg: 0-0.05%

The alloy usually contains no Mg. If it is added, Mg can reinforce the boundary between crystalline particles in a minute amount like B, Zr, and Hf as described above to increase the creep strength. This effect becomes significant when its content is 0.001% or more. However, if the content is more than 0.05%, the cleanness will degrade, and the ductility and the tenacity will deteriorate. Therefore, if it is added, the content of Mg is preferred to be in the range of 0.001-0.05%.

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[0042]

Mo: 0-6%, W: 0-12%

The alloy usually contains no Mo or W. If they are added, Mo and W will be mainly dissolved in the austenite phase to reinforce the austenite phase to increase the creep strength. This effect becomes significant when the content of M is 0.2% or more and when the content of W is 0.5% or more.

However, if the content of Mo is more than 6% or the content of Mo is more than 12%, intermetallic compound that will degrade the tenacity will be generated. Therefore, if they are added, the contents of Mo and W are preferred to be in the ranges of 0.2-6% and 0.5-12%, respectively.

[0043]

V: 0-3.5%

The alloy usually contains no V. If it is added, V will be dissolved in austenite phase or Cr carbide to improve the creep strength. This effect becomes significant when its content is 0.1% or more. However, when the content is more than 3.5%, the tenacity will degrade. Therefore, if it is added, the content of V is preferred to be in the range of 0.1-3.5%.

[0044]

Nb: 0-5.5%

The alloy usually contains no Nb. If it is added in a minute amount, Nb can increase the creep strength. This effect becomes significant when its content is 0.3% or more. However, if the content is more than 5.5%, the ductility and the tenacity will degrade. Therefore, if it is added, the content of Nb is preferred to be in the range of 0.3-5.5%.

[0045]

Ta: 0-11%

The alloy usually contains no Ta. If it is added in a minute amount, Ta can increase the creep strength. This effect becomes significant when its content is 0.5% or more. However, if the content is more than 5.5%, the ductility and the tenacity will degrade. Therefore, if it is added, the content of Ta is preferred to be in the range of 0.5-5.5%.

[0046]

Y: 0-0.25%, La: 0-0.25%, Ce: 0-0.25%

The alloy usually contains no Y, La, or Ce. If they are added, the main effect of said elements is to improve the adhesivity to SiO_2 or Al_2O_3 film under the thermal cycle conditions when the operation is stopped or started in chemical plant to maintain excellent anti-carburization property and anti-coking property even when the alloy is used at varying temperature. This effect becomes significant when the effect of any of said elements is 0.01% or more. However, if the content is more than 0.25%, the cleanness will degrade, and the processibility will deteriorate. As a result, [a usable] product may not be obtained in some cases. Therefore, if said elements are added, their content is preferred to be in the range of 0.01-0.25%.

[0047]

Bonding atmosphere

In order to restrain formation of oxide film during bonding, bonding is carried out in an active gas atmosphere containing 0-5% of H_2 or in a vacuum atmosphere of 8×10^{-1} torr or lower. When bonding is carried out in the inactive gas substance, the oxide film will be reduced. In order to further improve the

bonding property, it is preferred that said atmosphere contain at least 0.5% of H₂. Examples of inactive gas include Ar, N₂, etc.

[0048]

Bonding time

If the bonding retaining time is too short, the homogenization of the bonded part and the mother material cannot be well performed. As a result, it is not possible to obtain a bonding joint having good high-temperature strength. Consequently, it is necessary to retain [the bonding state] for at least 120 sec, preferably, 240 sec or longer. Although there is no upper limit, in consideration of the operation efficiency, said time should not be longer than 1800 sec.

[0049]

Pressure applied

If the pressure applied is lower than 0.1 kgf/mm², the Al₂O₃ oxide film on the bonding surface will not be broken, and satisfactory wettability cannot be obtained. On the other hand, if the pressure applied is higher than 2.0 kgf/mm², deformation tends to occur during bonding. Consequently, the pressure applied on the surface perpendicular to the bonding direction during bonding should be in the range of 0.1-2.0 kgf/mm², preferably, in the range of 0.3-1.5 kgf/mm².

[0050]

Post-heat treatment conditions

In the present invention, post-heat treatment is not required in order to obtain a joint with satisfactory high-temperature strength when said insertion material is used as said bonding conditions are satisfied.

However, as described above, if a post-heat treatment is performed to the joint part after bonding, the high-temperature strength can be further improved. Therefore, it is preferred to carry out a post-heat treatment.

[0051]

However, it is necessary to carry out the post heat treatment at a temperature T (°C) in the range of 1100-1350°C and under the condition that the value of parameter P derived from the equation below using temperature T and retaining time t (s) is 33 or smaller. If the temperature T is lower than 1100°C, the retaining time t becomes longer, and the efficiency becomes lower. If the temperature T is higher than 1350°C or parameter P is larger than 33, Ni-Al type intermetallic compound will be deposited in a large amount. As a result, the high-temperature strength (creep strength) will deteriorate significantly, and the tenacity will degrade.

[0052]

Although there is no need to specify the lower limit of parameter P, if P value is smaller than 25, the texture cannot be well homogenized. As a result, the high-temperature strength (creep strength) cannot be well improved. Consequently, the lower limit of the P value is preferred to be 25 or more.

[0053]

$$P = (T + 273) \times (\log(t/3600) + 20) \times 10^{-3}$$

Here, log means logarithm with a base of 10.

[0054]

Application examples

In the following, the effects of the present invention will be explained with reference to application examples.

[0055]

Table 1 shows the chemical composition of the material to bond (Ni-based alloy having a high Al content) used.

[0056]

TABLE 1

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①	合金	化 学 组 成 (重量%)																②
		C	Si	Mn	Cr	Fe	Al	Ni	Zr	Bf	Ti	Mo	Nb	V	Re	Te		
①	0.07	1.0	0.13	12.4	5.2	14.2	0.025	0.25	0.43	0.42	0.302	-	-	-	-	-		
②	0.03	0.5	0.08	17.3	1.9	7.1	0.022	0.03	0.44	0.56	0.106	4.1	5.4	-	-	-		
③	0.05	0.1	0.20	19.8	2.2	4.2	0.021	0.06	0.22	0.42	0.033	-	-	1.1	2.9	4.4		

Note) Remainder includes Ni and inevitable impurities.

- Key: 1 Alloy No.
- 2 Chemical composition (wt%)

[0057]

Table 2 shows the 10,000-h creep breakage strength of the material to bond at 1000°C. The creep breakage strengths of alloy No. (1), (2), and (3) are 1.3, 1.4, and 1.5 kgf/mm², respectively.

[0058]

TABLE 2

①	1000℃、10000hでの クリープ破断強度 (kgf/cm ²)	②
①	1.6	
②	1.4	
③	1.3	

Key: 1 Alloy No.

2 10,000-h creep breakage strength at 1000°C

[0059]

Table 3 shows the chemical composition of the insertion material of 10 types for the present invention and 6 types for the comparative examples.

[0060]

TABLE 3

1	2	3								4
		成分	Cr	B	Zr	Hf	Nb	Ta	Se	
5	本発明例	A1	8.1	3.0	—	—	—	—	1.1	1054
		A2	2.3	5.2	—	7.0	—	—	0.5	1092
		A3	5.4	2.9	—	2.3	10.1	4.1	2.1	1057
		A4	12.6	3.1	0.1	2.0	—	—	0.05	1026
		A5	17.8	2.4	4.2	—	7.8	12.4	2.9	1046
		A6	3.1	1.1	—	0.1	—	5.5	1.0	1082
		A7	3.2	4.7	5.0	6.5	1.6	—	4.0	1031
		A8	3.0	3.9	10.1	—	0.1	—	0.02	1058
		A9	3.2	2.7	3.4	—	8.0	7.4	2.9	1044
		A10	3.1	2.9	—	0.9	5.4	—	4.0	1040
6	比較例	B1	15.1	3.7	—	—	—	—	—	1042
		B2	3.0	3.2	—	0.05	—	1.2	2.2	1008
		B3	12.2	0.1	1.0	—	1.2	2.3	3.1	1112
		B4	15.4	2.1	—	1.3	—	—	0.2	1055
		B5	12.5	4.2	0.2	5.5	—	—	4.1	1034
		B6	4.1	4.3	—	7.1	—	1.0	3.3	1013

Note 1) Remainder includes Ni and inevitable impurities.

Note 2) — means being out of the range specified in the present invention.

- Key: 1 Category
- 2 Insertion material No.
- 3 Chemical composition (wt%)
- 4 Melting point
- 5 Example of the present invention
- 6 Comparative example

[0061]

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Said materials to bond and insertion materials were used to perform bonding under various bonding conditions. The properties of the obtained joints were evaluated.

[0062]

Tables 4-7 show the bonding conditions of each test number.

[0063]

TABLE 4

①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪
試料番号	試料名	材料	雰囲気	温度 (°C)	時間 (hr)	圧力 (kgf/cm ²)	加熱速度 (°C/hr)	炉内時間 (hr)	炉内温度 (°C)	炉内圧力 (kgf/cm ²)
12	AJ1	A1	Ar	1250	120	1.0	1.0	8215 (825)	0	0
	AJ2	A2						8125 (815)	0	
	AJ3	A3						8210 (825)	0	
	AJ4	A4						8074 (815)	0	
	AJ5	A5						8185 (825)	0	
	AJ6	A6						8079 (815)	0	
	AJ7	A7						8453 (855)	0	
	AJ8	A8						8432 (855)	0	
	AJ9	A9						8231 (825)	0	
	AJ10	A10						8487 (855)	0	
	AJ11	A11						8717 (875)	0	
	AJ12	A12						8713 (875)	0	
12	AJ13	A13	Ar	1250	120	1.0	1.0	8625 (865)	0	0
	AJ14	A14						8689 (865)	0	
	AJ15	A15						8689 (865)	0	
	AJ16	A16						8781 (885)	0	
	AJ17	A17						8851 (895)	0	
	AJ18	A18						8811 (895)	0	
	AJ19	A19						8812 (895)	0	
	AJ20	A20						8813 (895)	0	
	AJ21	A21						8814 (895)	0	
	AJ22	A22						P1 8260 (825)	0	
	AJ23	A23						P2 8168 (815)	0	
	AJ24	A24						P3 8368 (825)	0	
12	AJ25	A25	Ar	1250	120	1.0	1.0	P4 8147 (815)	0	0
	AJ26	A26								
	AJ27	A27								
	AJ28	A28								
	AJ29	A29								
	AJ30	A30								
	AJ31	A31								
	AJ32	A32								
	AJ33	A33								
	AJ34	A34								
	AJ35	A35								
	AJ36	A36								

Note) Conditions of the post heat treatment

P1 : 1350°C×1hr (p=32) ,
P2 : 1250°C×1hr (p=38) ,
P3 : 1150°C×0.1hr (p=27) ,
P4 : 1100°C×0.01hr (p=25) .

Key: 1 Category
2 Test No.

- 3 Alloy No.
- 4 Insertion material No.
- 5 Bonding atmosphere
- 6 Bonding temperature (°C)
- 7 Bonding time (sec)
- 8 Pressure applied (kgf/mm³)
- 9 Post heat treatment
- 10 Creep breakage time (h)
- 11 Bonding defect (%)
- 12 Example of the present invention

[0064]

TABLE 5

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)			
区分	試番	合金No.	挿入材No.	雰囲気	接合温度(℃)	接合時間(秒)	加圧力(kgf/cm ²)	後熱処理	クリープ破断時間(hr)	接合欠陥率(%)			
比較例	BJ1	①	B1	Ar	1230	120	1.0	—	1004(10%)	41			
	BJ2		B2						2439(24%)	27			
	BJ3		B3						2197(22%)	33			
	BJ4		B4						741(7%)	53			
	BJ5		B5						2200(22%)	53			
	BJ6		B6			60	0.5		2181(22%)	34			
	BJ7								2744(27%)	26			
	BJ8		A1			30	0		2903(29%)	23			
	BJ9					120			50(1%)	91			
	BJ10								※				

Note 1) — means being out of the range specified in the present invention.

Note 1) Mark * means that no bonded joint was obtained, and it was unable to carry out the creep test.

- Key: 1 Category
- 2 Test No.
- 3 Alloy No.
- 4 Insertion material No.
- 5 Bonding atmosphere
- 6 Bonding temperature (°C)
- 7 Bonding time (sec)
- 8 Pressure applied (kgf/mm³)
- 9 Post heat treatment
- 10 Creep breakage time (hr)
- 11 Bonding defect (%)
- 12 Comparative example

[0065]

TABLE 6

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①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪
区分	試番	合金No.	挿入材No.	雰囲気 空気圧力 (torr)	溶合 温度 (°C)	溶合 時間 (秒)	加圧力 (kgf/mm ²)	後熱 処理	クリープ 破断時間 (hr)	接合 欠陥 (%)
⑫	AJ25	①	Al	8.0×10^{-1}	1230	120	1.0	—	8543 (85%)	0
	AJ27			1.0×10^{-1}					8881 (88%)	0
	BJ11			1					1187 (12%)	58
	BJ12			160					886 (9%)	51

Note) — means being out of the range specified in the present invention.

- Key: 1 Category

- 2 Test No.
- 3 Alloy No.
- 4 Insertion material No.
- 5 Bonding temperature (°C)
- 6 Bonding time (sec)
- 7 Pressure applied (kgf/mm³)
- 8 Post heat treatment
- 9 Creep breakage time (hr)
- 10 Bonding defect (%)
- 11 Example of the present invention
- 12 Comparative example

[0066]

TABLE 7

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
区分	試番	合金No.	挿入材No.	雰囲気 空気圧力 (terr)	接合 温度 (°C)	接合 時間 (秒)	加圧力 (kgf/mm ²)	後熱 処理	クリープ 破断時間 (hr)	接合 欠陥 (%)
(12)	比較例	BJ13	①	Ar	1230	120	1.0	FL	2676(27%)	0
		BJ14	①	Ar	1230	120	1.0	FL	2624(26%)	0

Note 1) Conditions of the post heat treatment

Note 2) — means being out of the range specified in the present invention.

- Key: 1 Category
- 2 Test No.
 - 3 Alloy No.

- 4 Insertion material No.
- 5 Bonding pressure
- 6 Bonding temperature (°C)
- 7 Bonding time (sec)
- 8 Pressure applied (kgf/mm³)
- 9 Post heat treatment
- 10 Creep breakage time (hr)
- 11 Bonding defect (%)
- 12 Comparative example

[0067]

The properties of the joint were evaluated by measuring the bonding defect (void) percentage on the cross section of the bonded part of the bonded joint. The bonding defect (void) percentage is defined as $\{(\text{length of void})/(\text{bonded part length})\} \times 100\%$. Only a joint with bonding defect percentage of 0% was considered qualified.

[0068]

Figure 1 shows the shape of the creep test sample and the dimension of each part. A test sample in the shape shown in Figure 1 was obtained from a joint bonded under the aforementioned conditions, and a creep breakage test was conducted under the conditions of temperature 1000°C, stress 1.5 kgf/mm². A joint reaching 80% or more of the creep breakage time of the mother material was considered qualified. The creep breakage time of the mother material was 104 h or longer under the conditions of temperature

1000°C, stress 1.5 kgf/mm². With 104 h used as judgment standard, if a breakage time of 8000 h or longer was obtained, the corresponding joint was considered qualified.

[0069]

The test results are shown in Tables 4-7.

[0070]

As can be seen from Table 4, in test No. AJ1-AJ25 with the insertion material and bonding conditions in the ranges specified in the present invention, joints free of bonding defect and having creep breakage strength of 80% or more of that of the mother material were obtained. In particular, in tests No. AJ22-AJ25 in which post heat treatment was carried out under the conditions specified in the present invention, joints with creep breakage strength of 90% or more of that of the mother material were obtained.

[0071]

On the other hand, as shown in Table 5, in test No. BJ1 or BJ4 of the comparative example, the insertion material contained no Zr, Hf, Nb, Ta, Ce at all or contained Ce in excessive amount. Therefore, the bonding defect percentage became 40% or higher, and the creep breakage strength was about 10% of that of the mother material. In test No. BJ2 or BJ3 of the comparative example, the B content in the insertion material was too high or too low. Therefore, both the bonding defect percentage and the creep breakage strength became poor. In test No. BJ5 or BJ6 of the comparative example, the Cr content in the insertion material was too high or too low. Therefore, said two characteristics became poor. In test No. BJ7 or BJ8 of the comparative example, since the bonding time was too short, said two characteristics

became poor. In test No. BJ9 of the comparative example, since bonding was performed with no pressure applied, the creep breakage strength was very poor. In test No. BJ10 of the comparative example, since the pressure applied was too high, no bonded joint was obtained, and it was not possible to carry out the creep test.

[0072]

As shown in Table 6, in tests No. AJ26 and AJ27 of the example of the present invention, satisfactory results were obtained for the aforementioned two characteristics. On the other hand, in test No. BJ11 and BJ12 of the comparative example, since bonding was performed at air pressure 1 torr or in the air, the creep breakage strength was low, and the bonding defect percentage was high.

[0073]

As shown in Table 7, in tests No. BJ12 and BJ14 of the comparative example, no bonding defect occurred. However, the parameter P value was 34 in the former case, while the temperature T was 1400°C in the latter case. Since the condition of the post-heat treatment was out of the range specified in the present invention, the creep breakage strength was very low.

[0074]

Effect of the invention

According to the present invention, Ni-based alloy having high Al content can be bonded without deteriorating the creep strength or other characteristics so that highly safe petrochemical plants can be built at low cost.

Brief description of figures

Figure 1 shows the shape of the creep test sample and the dimension of each part used in the creep test of the application examples.

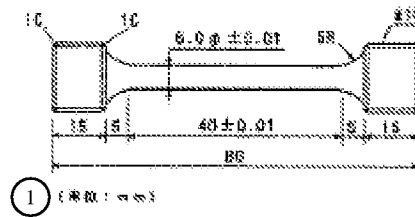


Figure 1

Key: 1 scale: mm